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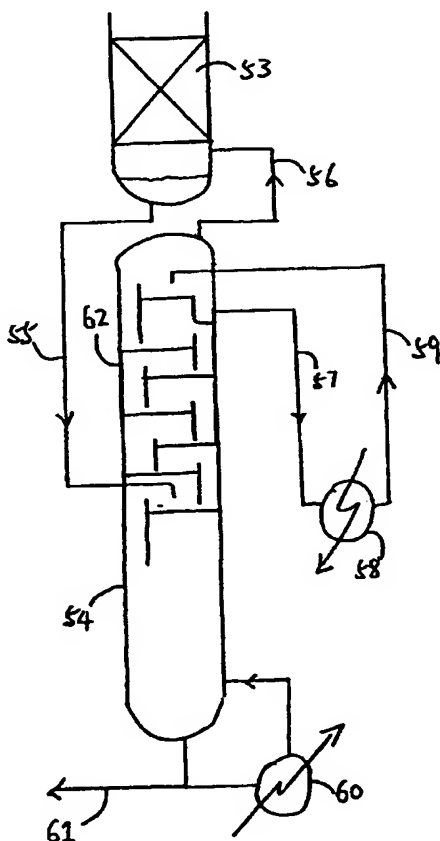
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(54) Title: NEW DIMENSIONS IN REACTIVE DISTILLATION TECHNOLOGY



(57) Abstract: A method of separating reactants from products within a reactive distillation structure (62). Reaction products heavier than reactants, such as ethylbenzene product with benzene and ethylene reactants are discouraged from re-entering the reaction zone (53) by introduction of a rectifying section (44) in between the reaction zone and the stripping section (47). Reaction products lighter than reactants, such as hydroconversion process, are discouraged from re-entering the reaction zone by introduction of a stripping section in between the reaction zone and the rectifying section.

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## **New Dimensions in Reactive Distillation Technology**

### **Background- Field of Invention**

This invention relates to reactive distillation, specifically to improvements in reaction selectivity and conversion, resulting in reduced catalyst volume and capital costs requirement.

### **Background-Discussion of Prior Art**

Combining chemical reaction and distillation in one unit operation has found more and more acceptance in numerous applications. This market trend is evident by the number of new installations and expansion projects coming on stream having gone the reactive distillation route. While this approach is becoming popular, there is some built in difficulty of combining the two said functions into one process structure. The main problem is pressure drop across the reaction zone.

In an attempt to overcome the physical limitations of fixed bed catalyst bed structure, the particulate catalyst in some columns has been placed into a plurality of pockets within a stainless steel cloth belt/bundle arrangement as in U.S. Pat. No. 4,242,530. The net effect is a creation of free paths for liquid / vapor counter current flow within the reaction zone. This lower pressure drop in the reaction zone is comparable to a conventional packed column, allowing the said reaction and separation operations to proceed to some degree of success. Other patents following the same concepts that deals with pressure drop reductions have been well documented as in structured packing U.S. Pat No. 5,073,236 and others such as U.S. Pat. No. 4,439,350 using alternating fixed structures to hold catalysts in place. They all focus on minimizing pressure drop in the reaction zone while providing the necessary catalyst volume to perform a given conversion requirement.

A closer look at the reaction zone reviews two major drawbacks in such an arrangement:

- 1) Because of the free paths available, by definition, both the reactants and the products are free to move into the reaction area or choose to remain in the vapor / liquid main stream free area. Since there is no provision of separation of product(s) from reactant(s) within the reaction zone, both yield and selectivity suffer when compared to a conventional fixed bed reactor coupled with down stream separation unit, such as MTBE processes taught by U.S. Pat. No. 4,198,530. The catalyst beds in reactive distillation are often longer in dimension by necessity so as to keep up with the same degree of conversion. In other words, longer

residence time will be required. Unfortunately, this higher residence time could cause further loss in reaction selectivity as desirable product(s) has more time to be converted to undesirable by-products.

2) A portion of the product(s) leaving the reaction zone is being returned back into the reaction zone; either by vapor entering the reaction zone from the bottom in the case of product(s) having a higher boiling point than the reactant(s) such as ethyl benzene from ethylene and benzene U.S. Pat. No. 5,476,978; or by liquid entering the reaction zone from the top in the case of product(s) having a lower boiling point than the reactant(s) such as hydroconversion process U.S. Pat No. 5,961,815. These inefficiencies are built-in as the liquid leaving the reaction zone containing the product(s) is approaching thermodynamic equilibrium with the vapor rising from the tray below. The same is true for the product(s) leaving the reaction zone as vapor from the top of the reaction zone. It comes into intimate contact with the liquid at the tray just above the reaction zone and the two streams are approaching thermodynamic equilibrium. Besides the thermodynamic and fluid dynamic limitations, the cost of such special arrangements of catalyst such as structured packing type catalyst would obviously be a decision factor. Efforts to minimize catalyst bed volume would improve the competitiveness of reactive distillation.

### **Objects and Advantages**

Accordingly, several objects and advantages of my invention are:

The present invention focuses on the re-entering of products into the reaction zone and provides a positive way of separating the products from the reactants. This allows the chemical reaction to proceed with high degree of selectivity. The two factors that are responsible for this enhancement are:

Firstly, amounts of products that re-enter the reaction zone can be manipulated and optimized, and that discourages secondary reactions which produce unwanted by-products and,

Secondly, the reduced amount of products re-entering the reaction also leads to overall lower product concentration throughout the reaction zone. Equilibrium reaction is encouraged to proceed from reactants to the desirable products.

It follows that the two factors above would enable a shorter residence time of reactants in the reaction zone as compared to the conventional reactive distillation arrangements and still provide the same or better conversion rate. That leads to possibility such as having much shorter bed amongst others.

The above revelations open up yet another dimension in the field of reactive distillation. Further objects and advantages of my invention will become apparent from a consideration of drawings and ensuing description.

### **Description of Drawings**

Fig. 1a shows the basic concepts of multiple flash and liquid vapor phase equilibrium.

Fig. 1b shows the effect of staged flashing, the principal behind distillation column.

Fig. 1c shows feed location, rectifying section and stripping sections of a typical column.

Fig. 1d shows three connected flash drums representing a distillation functional structure.

Fig. 2a shows heat removal using pumparound.

Fig. 2b shows heat removal using partial condenser.

Fig. 2c shows heat removal using condenser coil placed inside a column.

Fig. 3a shows heat addition using side reboiler.  
Fig. 3b shows heat addition using heater coil inside column.  
Fig. 4a shows the preferred embodiment of providing rectification in reactive distillation.  
Fig. 4b shows the preferred embodiment of providing stripping in reactive distillation.  
Fig. 5a shows an alternate arrangement of providing rectification in reactive distillation.  
Fig. 5b shows an alternate arrangement of providing stripping in reactive distillation.

**List of Reference Numerals**

- 1 First chamber to hold 50/50 liquid BZ and EB.
- 2 Liquid BZ and EB 50/50.
- 3 Vapor BZ and EB 55/45.
- 4 Liquid / vapor interphase.
- 5 Same first chamber, 1 above.
- 6 Second chamber.
- 7 Vapor from first chamber, 55/45 BZ to EB.
- 8 Totally condensed vapor from first chamber.
- 9 Condenser.
- 10 Heater coil.
- 11 Liquid BZ and EB 55/45.
- 12 Vapor BZ and EB 59/41.
- 13 Typical distillation column.
- 14 Overhead vapor.
- 15 Overhead condenser.
- 16 Reflux accumulator drum.
- 17 Reflux flow.
- 18 Distillate product.
- 19 Rectifying section.
- 20 Stripping section.
- 21 Feed to the column.
- 22 Bottom product.
- 23 Reboiler vapor return.
- 24 Reboiler.
- 25 Flash drums.
- 26 Condensers.
- 27 Heater coils submerged in liquid.
- 28 Vapor from first flash drum.
- 29 Condensed vapor from first flash drum.
- 30 Return liquid from second flash drum.
- 31 Vapor from second flash drum.
- 32 Condensed vapor from second flash drum.
- 33 Return liquid from third flash drum.
- 34 Raffinate product.
- 35 Bottoms.
- 36 Feed.
- 37 Total draw off from tray.
- 38 Heat exchanger to cool tray draw off.
- 39 Cooled liquid being returned to column, 37, 38 & 39 called pumparound.
- 40 Vapor from vapor phase of a tray.
- 41 Partial condenser.

- 42 Two phase flow with liquid and vapor return.
- 43 Condenser coil in vapor phase.
- 44 Rectifying section of the column.
- 45 Feed to the column.
- 46 Feed to the column.
- 47 Stripping section of the column.
- 48 Total liquid draw off from the column.
- 49 Partially vaporized return flow to the column.
- 50 Side reboiler.
- 51 Downcommer.
- 52 Submersed heater coil in liquid phase.
- 53 Reaction zone producing heavier products than reactants.
- 54 Stripping section below reaction zone.
- 55 Liquid from reaction zone bypasses RRD.
- 56 Vapor to reaction zone from RRD.
- 57 Liquid pumparound from column.
- 58 Cooler.
- 59 Cooler pumparound return.
- 60 Reboiler.
- 61 Product to be further separated.
- 62 Rectified reactive distillation, RRD.
- 63 Rectifying section above reaction zone.
- 64 Stripped reactive distillation, SRD.
- 65 Vapor from reaction zone bypasses SRD.
- 66 Reboiler for stripping.
- 67 Liquid to reboiler.
- 68 Vapor and liquid return to SRD.
- 69 Stripped liquid flow from SRD to reaction zone.
- 70 Overhead condenser.
- 71 Distillate product to be further separated.
- 72 Reaction zone.
- 73 Stripping zone.
- 74 Vapor from stripping zone to RRD unit.
- 75 Liquid from reaction zone.
- 76 Condensed vapor in rectifying section.
- 77 Vapor to condenser.
- 78 Vapor to reaction zone.
- 79 Condenser.
- 80 Liquid from RRD unit returning to stripping zone.
- 81 Rectification section, trayed or packed column, RRD unit.
- 82 Stripped product.
- 83 Reaction zone.
- 84 Vapor from reaction zone.
- 85 Rectification zone.
- 86 Condenser.
- 87 Reflux.
- 88 Distillate product.
- 89 Vapor from SRD unit returning to rectification zone.
- 90 Liquid from rectification zone to SRD unit.

- 91 Stripped liquid from SRD unit to reaction zone.
- 92 Reboiler.
- 93 Stripping section, trayed or packed column, SRD unit.

### Summary

The summary of my invention is a method of separating reaction products from reactants within a reactive distillation structure by providing rectification and / or stripping capabilities below and / or above the reaction zone, respectively, whereby the amount of reaction products re-entering the said reaction zone can be manipulated. The said reaction zone enhancement directly results in reduced reactor bed height requirement. Indirectly, this invention offers an added dimension in optimizing process design in reactive distillation.

### Description of Invention

#### BACKGROUND

In order to appreciate the level of innovation of the present invention, one must approach the subject with very thorough understanding of phase equilibrium. The configuration of a typical distillation column cannot be taken for granted. Let us use benzene / ethyl benzene as an example of a binary system. See Fig. 1a.

Of the two components, benzene (BZ) is lighter than ethyl benzene (EB) as the vapor pressure of BZ is higher than EB at any given temperature. Given a binary system of BZ and EB in contact with each other, say a 50/50 mix, each component will exert its own vapor pressure above the mixed liquid. From vapor pressure law, partial pressures and mole fractions, it follows that the mole fraction of the lighter component (BZ) will be higher in the vapor phase than in the liquid phase. It also follows that the heavier component (EB) will have a lower mole fraction in the vapor phase by difference. If the vapor above this liquid were to be condensed to form a second liquid phase in another chamber, the liquid mole fractions has to be the same as the vapor that comes from the former chamber. See Fig. 1b. Flashing this liquid will yield the same phenomenon as in the liquid in the former chamber. This RELATIVE VOLATILITY, as often used in distillation jargon, determines the degree of difficulty in separating a stream with mixed components into two separate streams; one having more concentrated light components and the other more heavy components.

Distillation column arrangement is a very elegant way of taking advantage of liquid flowing downwards and vapor flowing upwards in a series of multiple flashes. See Fig. 1c. The arrangement eliminates external inter-stage heat addition to re-vaporize the condensed vapor and external inter-stage heat removal to re-condense the vaporized liquid as heats are internally reused from tray to tray. The feed generally enters the column at a location where the feed enthalpy and composition minimizes energy for a given separation requirement. The section above the feed point is commonly known as the rectification section while the section below, the stripping section. RECTIFICATION cleans up the lighter stream, often called the distillate, by removing the heavy ends. STRIPPING strips the light ends out of the heavier stream, often called the bottom, and makes it purer.

One must not limit the application of such fundamental principles to a traditional distillation column structure as shown in Fig. 1c. Fig. 1d is also a distillation column arrangement even though it consists of three sets of equipment and does not resemble a conventional

distillation column. For the purpose of this Specification, Fig. 1d is a form of DISTILLATION FUNCTIONAL STRUCTURE that embodies the principal of multiple flashes and relative volatility. Other examples of DISTILLATION FUNCTIONAL STRUCTURE can be found in U.S. Pat. No. 4,978,807 where the reaction zone 'above' and the distillation section 'below' are joined by lines that carry process fluids from one vessel to another and function as one reactive distillation structure.

In some cases, too much heat is experienced in a specific zone, such as often seen in crude unit distillation. PUMPAROUNDS are often used to remove heat locally so that a more economical design can be reached in the rectifying section. In other cases, heats are added mid stream by the use of SIDE REBOILERS in the stripping section to balance vapor loading in order to increase capacity, as in ethylene fractionation. These two scenarios are not to be confused with the present invention. As there is a certain degree of perceived similarity between the present invention and the traditional PUMPAROUNDS and SIDE REBOILERS, it is necessary to fully explain the two traditional use of heat removal (PUMPAROUND) and heat addition (SIDE REBOILER) devices.

**PUMPAROUNDS** As in Fig. 2a, the liquid from one tray is being drawn to heat exchange with a cooler stream. The liquid is then returned, at a lower temperature, back to the column. If the return location is at the same tray, there is no loss in mass transfer function. In simple terms, no back mixing. If the return location is above the draw tray, then the trays in between no longer perform mass transfer function. They are called heat transfer trays instead. It is because by returning a stream of heavier components to a higher location in the column, all the trays in between will be at the same composition profile. Heat removal can be accomplished in other ways such as partial vapor condensation as in Fig. 2b or even with a condenser coil inside the column as in Fig. 2c. All these plus others available on the market are for the purpose of heat removal.

**SIDE REBOILERS** As in Fig. 3a, the liquid from a tray can be drawn off to a heat exchanger where heat is added to the stream. The stream can be returned either to the same tray, one tray above or one tray below. In theory, it is most efficient to return the vapor to the tray above and the liquid to the tray below as the side reboiler flashes the stream into lighter vapor and heavier liquid for relative volatility reasoning as mentioned earlier. In practice, however, most side reboiler returns the flashed stream to a disengaging space one tray below the draw tray. Heat can be added in other ways such as a submerged heater on the tray, Fig. 3b. Thermal siphons are often used in side reboiler applications. Regardless, heat added will result in additional vapor being generated.

#### PRESENT INVENTION

Let us examine the configuration as in Fig. 4a. This arrangement, defined as rectified reactive distillation (RRD), provides rectification capability below the reaction zone. The products of reaction, being heavier than the reactants, now by-pass this rectification zone and re-enters the column via liquid stream 55. The vapor arising from below no doubt will vaporize some of this heavier product back up the column. However, the rectification section prevents large amounts of product from re-entering the reaction zone. At the same time, allows the lighter reactants to re-enter the reaction zone. This arrangement provides a direct method of separating products from reactants as soon as products and reactants leave the reaction zone. Such superior technical capability is not found in any conventional reactive distillation system presently being offered on the market. Alternatively, the

rectification function can also be provided by a separate column, trayed or packed, as shown in Fig. 5a. Here, the vapor from the stripping section below the reaction zone is now rectified before re-entering into the reaction zone. Those skilled in the art would be able to come up with many other arrangements bearing the same principles of a RRD in other DISTILLATION FUNCTIONAL STRUCTURES as defined earlier.

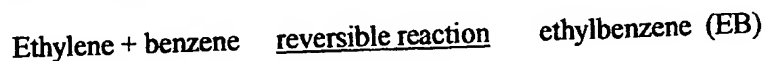
Let us examine the configuration as in Fig. 4b. This arrangement, defined as stripped reactive distillation (SRD), allows an added zone for stripping above the reaction zone. The products of reaction, being lighter than the reactants in this case, now by-pass this stripping zone and re-enters the column via stream 65 to be rectified. The liquid reflux from the top no doubt will condense some of this lighter product back down the column. However, this added stripping section will selectively strip out the lighter components in the internal liquid traffic. That puts a lid on the amount of products already made re-entering the reaction zone while allowing heavier components to go down to the reaction zone to get re-cracked and make desirable products. This arrangement, again, provides a direct method of separating products from reactants as soon as products and reactants leave the reaction zone. Such superior technical capability is again not found in any conventional reactive distillation system presently being offered on the market. Alternatively, the stripping function can also be provided by a separate column, trayed or packed, as shown in Fig. 5b. Here, the liquid from the rectifying section above the reaction zone is now stripped before re-entering into the reaction zone. Those skilled in the art would be able to come up with many other arrangements bearing the same principles of a SRD in other DISTILLATION FUNCTIONAL STRUCTURES as defined earlier.

The implication of both the RRD and SRD, together named after the inventor as the "TUNG'S arrangements", are more far reaching than apparent. They can provide another dimension in reactive distillation design. To begin with, let us first examine the effect of RRD on ethylene and benzene to make ethyl benzene reaction as an example.

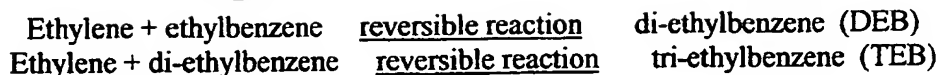
### Additional Ramifications

The use of a catalyst packed distillation column allows concurrent catalytic reaction of reactant(s) and fractionation of the product(s) from the reactants all in one step. The use of solid, particulate catalysts in a conventional fixed bed reactor within such a distillation column usually results in high pressure drop within the column because of the lack of free paths available for liquid / vapor counter current flow. Pressure drop increases as the bed ages, caused by compaction and breakage of the catalyst, further make this arrangement undesirable due to maintenance requirements and result in down time. If not maintained regularly, channeling and hot zones would cause severe selectivity, yield and capacity penalties. One solution was offered by the following Patent to deal with the pressure drop issue but in so doing, knowingly or unknowingly, have paid a stiff penalty on conversion, selectivity, capital and operating costs.

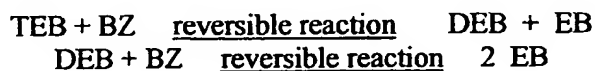
As taught in U.S. Pat. No. 5,476,978, a large benzene recycle of up to 100:1 benzene to ethylene ratio, is recommended to minimize side reaction of di-ethylbenzene (DEB), tri-ethyl benzene (TEB) and poly-ethylbenzene (PEB), all collectively known as polyalkylates formation. The following is the chemical reaction:







Another way of looking at the function of benzene recycle is the lowering of ethyl benzene (EB) to benzene (BZ) ratio so that a fresh ethylene molecule has a better chance of pairing up with BZ than with EB. However, even with the overwhelming numbering advantageous scheme of BZ over EB in the reaction zone, PEB's are still formed in large enough amounts so as to warrant the design of a transalkylator system. The transalkylator system is for the conversion of PEB's back to EB by adding BZ.



In fact, a large portion of the specification dealt with the re-conversion of the PEB by-products back to the desirable product of EB. This again adds extra recycling load of reprocessing and is very energy inefficient. Operating costs and capital equipment depreciation make this process less attractive. Had a RRD been incorporated into the design, the reaction zone can be made to optimize the quantity of EB returning from the stripping section below. This reduces the EB concentration all across the reaction zone, especially where the ethylene is being injected. Besides limiting undesirable secondary side reactions, lower EB concentration works very favorably towards shifting the equilibrium towards the product side, producing EB as the reaction product. EB, once made, would again be readily removed in an efficient and timely manner. The above two steps would repeat and feed on each other. In addition, a very shallow penetration of the reaction zone will result which again aids product removal as EB need not travel too far into the reaction zone before being removed. The overall effects would be reduced reactor catalyst volume requirement and benzene recycle flow, and may even challenge the need for the transalkylator system. With the present invention, a truly efficient reactive distillation set-up is on hand. For an existing reactive distillation design using said prior art technology, the present invention can be a huge boost to profit margin. Besides, retrofitting costs could be paid off by a few weeks of using RRD. The following process simulation exercise using CHEMCAD software illustrates the impact of an RRD, retrofitted.

Table 1

Stream	Temperature, deg F	Flow rate, lb/hr	Location	BZ/EB, mass ratio	Duty, MMBTU/hr
Feed, F-1	440	10,000	Tray 1	1.00	
Distillate, D-1	440	5,240	Tray 1	2.27	
Bottom, B-1	474	4,760	Tray 10	0.40	0.70
Feed, F-2	440	10,000	Tray 6	1.00	-0.50
Distillate, D-2	417	3,560	Tray 1	7.85	
Bottom, B-2	474	6,440	Tray 10	0.40	1.00

The above simulation results, using SRK thermodynamic data, highlights the effect of a RRD unit within a 10 stage stripping section. The actual benefit will be more pronounced when the secondary effects, by iterative steps of substituting the calculated vapor's impact on entering liquid, are accounted for. It is for illustration purpose only.

The base case, case 1, simulates a bubble point liquid stream, F-1, enters a conventional

reactive distillation stripping section from the reaction zone above. F-1 has a 50/50 mix of BZ and EB. The bottom target is maintained at BZ/EB ratio of 0.40 for further down stream product recovery. Reboiler duty is calculated by the program to be 0.70 MMBTU/hr, and D-1 contains 2.27 BZ/EB ratio. This ratio tells us that 30% of the vapor returning to the reactive distillation zone is actually EB!

The comparison case, case 2, starts with the same feed, but named F-2 for clarity. The bottom concentration is fixed at the same BZ/EB ratio of 0.40 and the reactor effluent flow is by-passed to 5 trays lower in the stripping section of the column. Please note that no additional staging is provided to show the attractiveness of retrofitting existing systems. Condenser duty is arbitrarily chosen at 0.5 MMBTU/hr and the program calculates the rest of the information. Notice the distillate, D-2, has gone up to 7.85 BZ/EB ratio. That is 3.5 times purer than case 1. Also, more bottom flows are achieved, accounting for a lower net rate of EB back into the reaction zone. The above is an illustration of the impact of RRD on reactive distillation.

As taught in U.S. Pat. No. 5,961,815, hydrogen is fed at a point below the heavy petroliferous stock boiling above 400 deg F where a reactive distillation arrangement generates lighter, more desirable products. It would be easy to see that quite a bit of desirable products will re-enter the cracking zone, causing more light ends to form and losing out on overall reaction selectivity. Had a SRD been incorporated into the design, it will limit the reaction zone from re-cracking the desirable products, such as gasoline cut, from the reflux stream. This will drastically improve overall cracking selectivity and make better use of hydrogen, which is usually short in a refinery environment. Those skilled in the art would have no problem simulating the effect of a SRD as demonstrated by the approach as in Table 1 above and come to a similar conclusion.

As taught in U.S. Pat. No. 5,118,873, Process for the Preparation of MTBE, an external inert butane source is being added to a reactive distillation structure in order to affect the methanol / butane azeotrope. Methanol and butane form an azeotrope, which effectively enables methanol to boil at a lower temperature. So does methanol and iso-butylene. In this application, an essentially pure stream of iso-butylene is used. So once the iso-butylene has been reacted, iso-butylene is no longer available to form the azeotrope. Methanol is heavier than both butane and iso-butylene and will tend to fractionate to the bottom of the column. Methanol / butane azeotrope is therefore the tool used to lift methanol back into the reaction zone. This Patent deals with the challenge of balancing the inert butane profile within the reactive distillation structure. In Fig. 2 of the said patent, butane is added for the azeotrope forming purpose. Provisions are also made to strip out the excess butane by the introduction of a down stream stripper in order to limit vapor loading in the main distillation zone. At first glance, the above configuration may appear to share some remote similarity with the present invention. However, its design intent and functionality bears no relevance to the present invention. In fact, a RRD can be retrofitted in this example to again rectify the MTBE rich vapor stream and allow better conversion rates than this Patent currently offers.

Another spin-off of the efficient product removal is the ability to design multiple reaction zones, each performing a different reaction task and benefiting from the re-use of heat and properly separated reactants. For example, if ethylbenzene needs to be further converted to, say an alkyl-ethylbenzene as a preferred final product, the reaction can now be carried out in a two step process in the same distillation column. RRD's can be placed where rectification is required to enhance reaction selectivity as in the single reactive distillation case.

It is important to note that reactive distillation covers a much wider range than catalytic distillation. That is because catalysts, as we commonly refer to, are usually in the form of solid pellets. In this invention, reactive distillation is defined as a distillation functional structure that facilitates a reaction. Generally, solid catalysts function as providing active sites by forming intermediate complexes with the reactants. This physical / chemical adsorption step lowers the activation energy of the reaction, and starts the chemical reaction to reach its chemical equilibrium. It is one way of encouraging a chemical reaction to go forward. In cases of reversible chemical reactions, the lowering of activation energy equally allows the reverse reaction to proceed.

Any of the following, plus others, can also initiate a reaction:

Heat, ionizing beam, initiators such as injection of oxidizing agents, high energy beam like ultra violent radiation, enzymatic and so on.

In short, once the reaction system overcomes the activation energy barrier, the true limitation is the chemical equilibrium. This chemical equilibrium is commonly defined as forward reaction rate divided by reverse reaction rate. That is why the efficient removal of products in a reaction zone ultimately determines the success of any reaction system design.

### **Conclusion, Ramifications, and Scope of Invention**

Thus the reader will see that this invention is truly the missing link in reactive distillation technology. The reaction zone, as illustrated in the above specification, can be viewed as an example. The invention carries further than the reaction zone boundary. A zone that carries out an operation that affects some form of different output than the input given can also be applicable to this invention. For this reason, the term operating zone is defined. In essence, the present invention provides a break in the composition profile continuum which otherwise cannot be achieved. In writing this specification, a cross-disciplinary approach has been taken to explain the invention. While my above description contain many specificities, these should not be construed as limitations on the scope of the invention, but rather as exemplification on one preferred embodiment thereof. Many other variations are possible. Examples can be found in coal tar distillation, biotechnology, and pharmaceutical manufacturing processes and food and beverage applications and the list goes on.

## Claims

What is claimed as the invention is:

1. A method of separating at least one product from at least one reactant comprising of a distillation functional structure, at least one operating zone and a means of providing rectification below said operating zone, whereby manipulation of said product and said reactant re-entering the operating zone can be achieved,
2. The method according to claim 1, wherein said distillation functional structure is a distillation column,
3. The method according to claim 1, wherein said distillation functional structure is a reactive distillation column,
4. The method according to claim 1, wherein said operating zone contains at least one reaction zone,
5. The method according to claim 4, wherein said reaction zone contains catalysts,
6. The method according to claim 4, wherein said rectification below the reaction zone is provided by the use of a pumparound immediately below said reaction zone,
7. The method according to claim 4, wherein liquid from said reaction zone bypasses said rectification section and re-enters said distillation functional structure,
8. A method of separating at least one product from at least one reactant comprising of a distillation functional structure, at least one operating zone and a means of providing stripping above said operating zone, whereby manipulation of said product and said reactant re-entering the operating zone can be achieved,
9. The method according to claim 8, wherein said distillation functional structure is a distillation column,
10. The method according to claim 8, wherein said distillation functional structure is a reactive distillation column,
11. The method according to claim 8, wherein said operating zone contains at least one reaction zone,
12. The method according to claim 11, wherein said reaction zone contains catalysts,
13. The method according to claim 11, wherein said stripping above the reaction zone is provided by the use of a side reboiler immediately above the reaction zone,
14. The method according to claim 11, wherein vapor from said reaction zone bypasses said stripping section and re-enters said distillation functional structure.

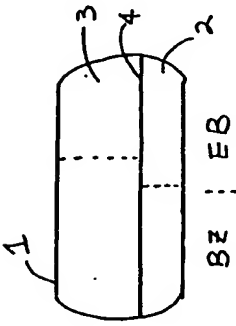


FIG. 1a

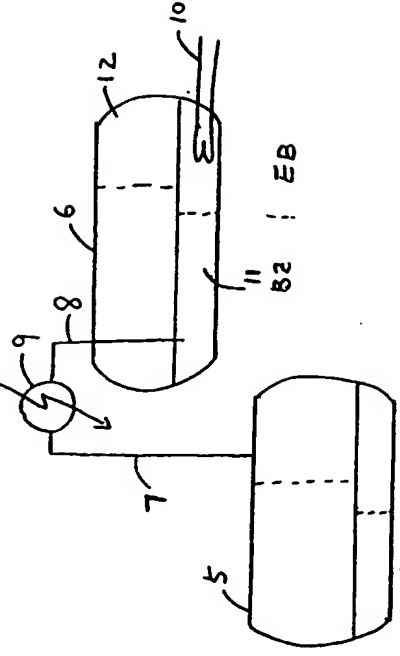


FIG. 1b

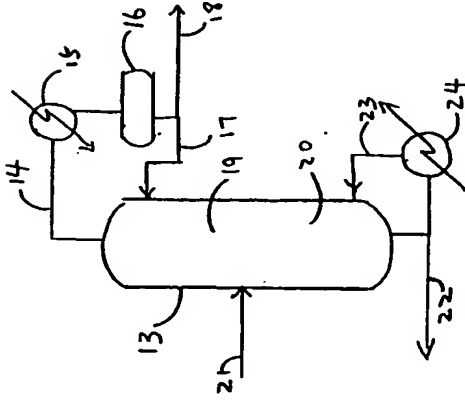


FIG. 1c

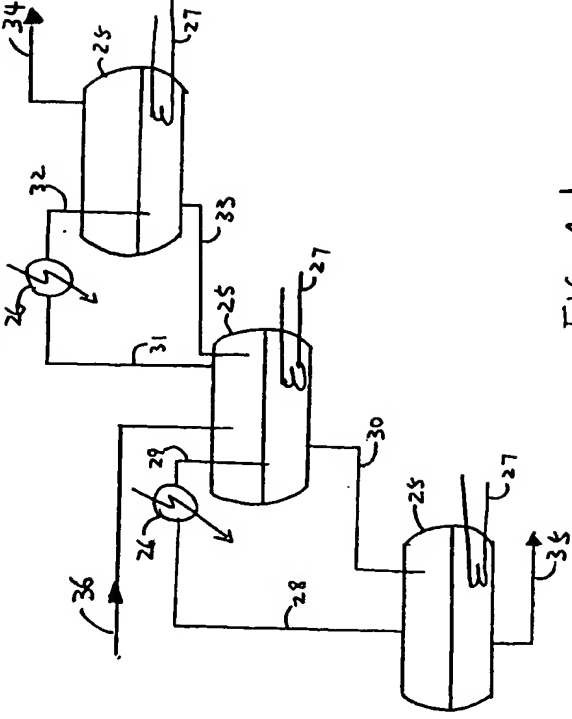


FIG. 1d

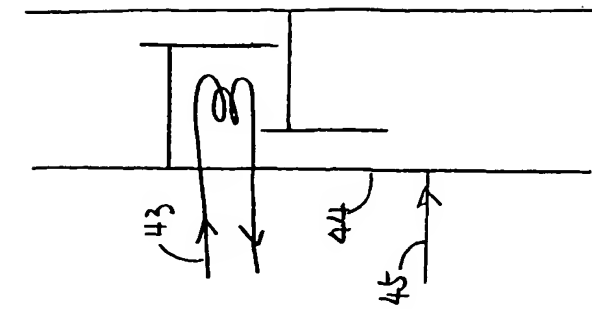


FIG. 2C.

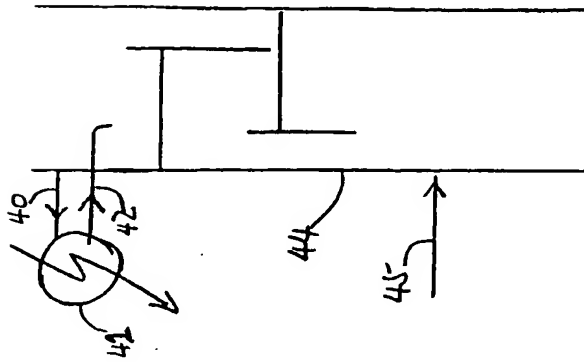


FIG 2b

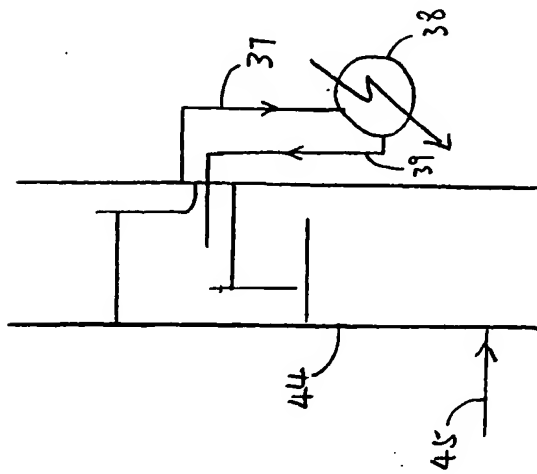


FIG 2a

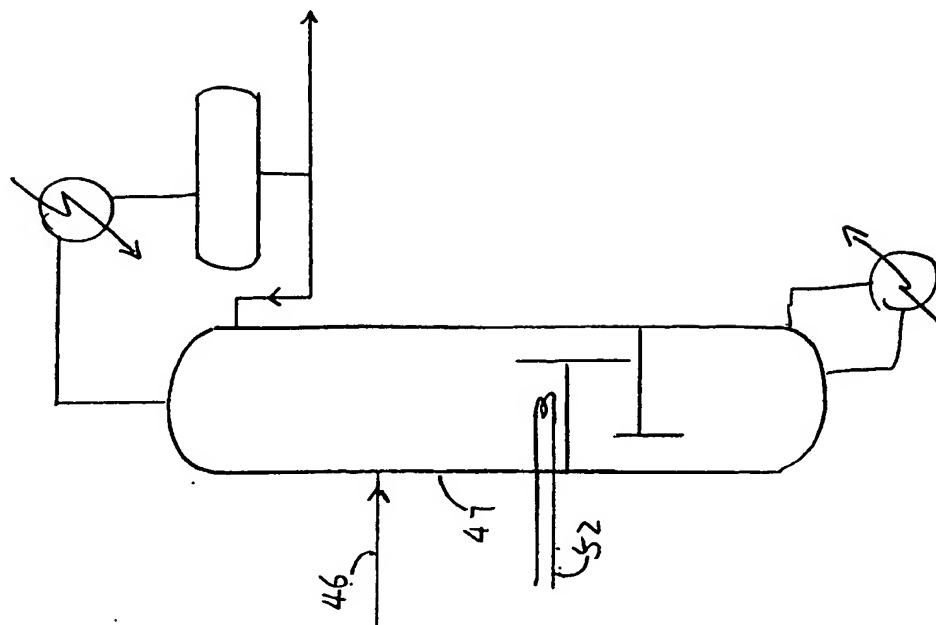


FIG 3b

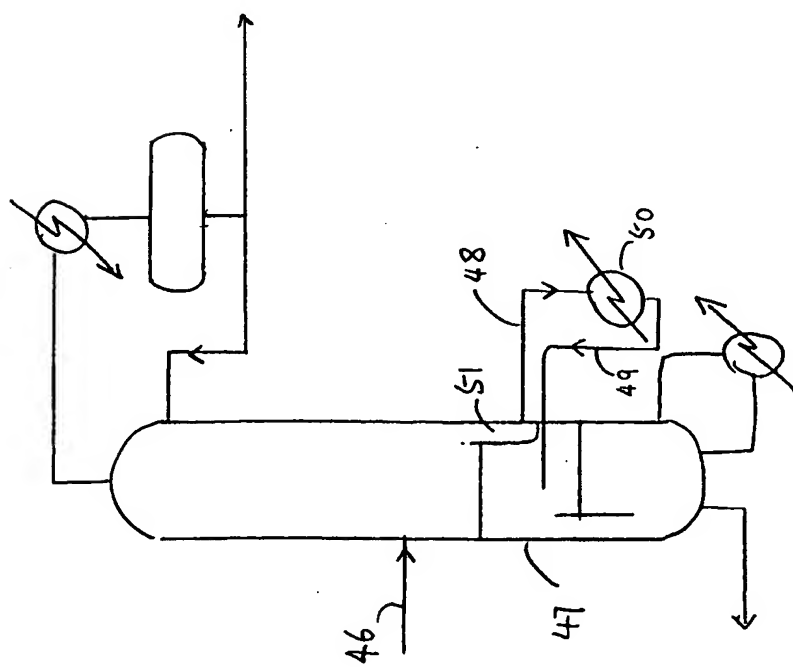


FIG 3a

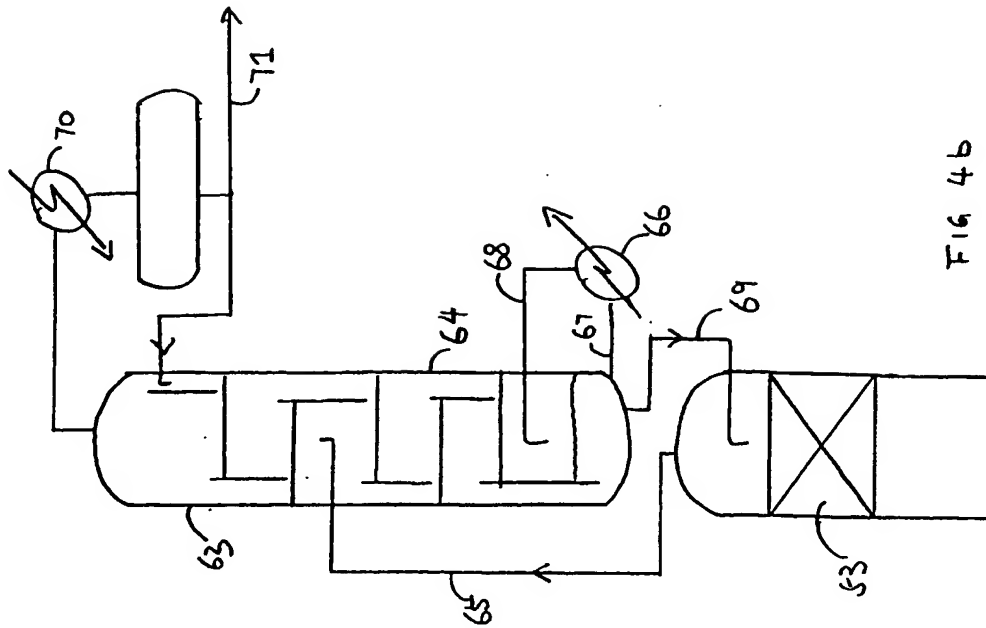


Fig 4b

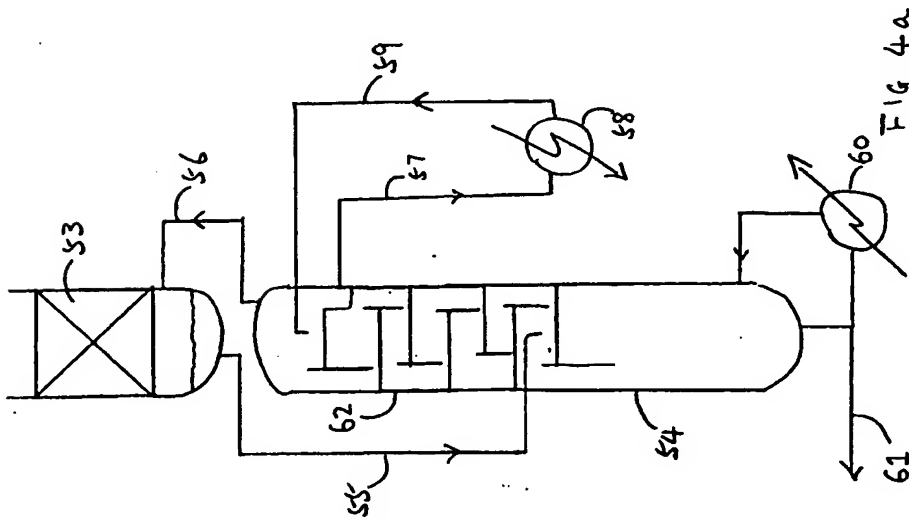


Fig 4a



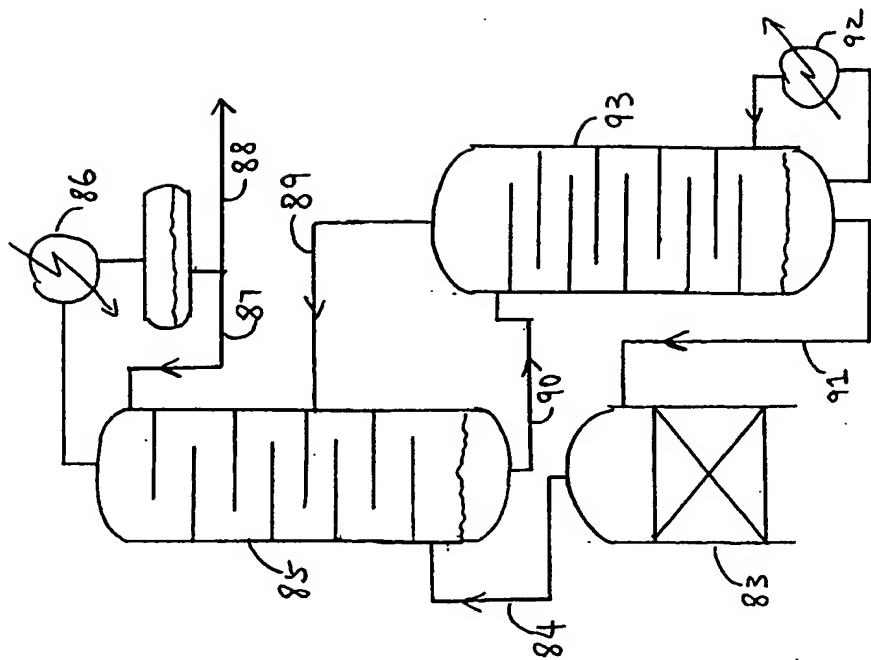


FIG. 5b

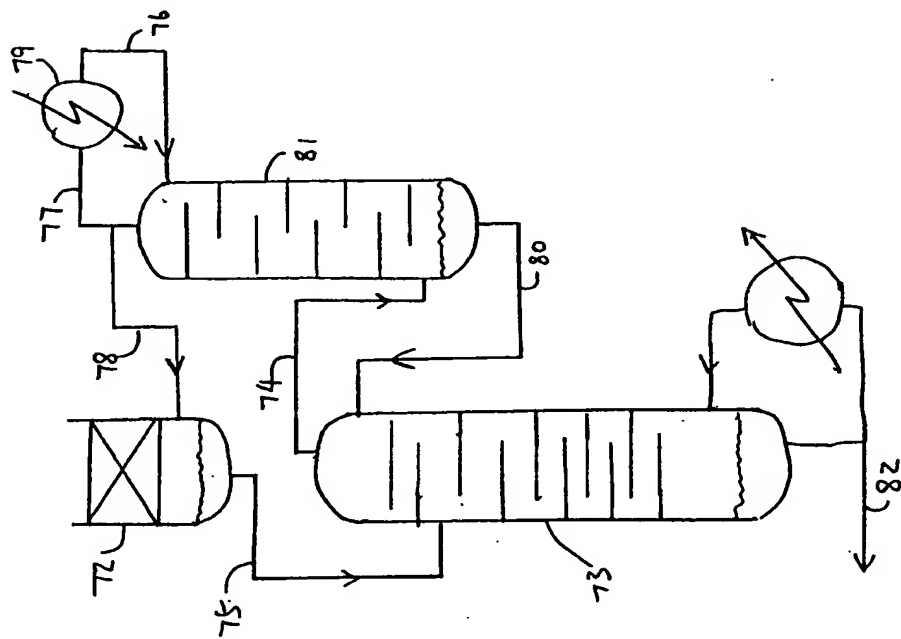


FIG. 5a

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US00/33327

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 3/00, 3/32, 3/42; B01J 8/02; C07C 2/66, 7/04

US CL : 203/29, 98, DIG.6; 422/193, 213; 585/467, 805

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 203/1, 3, 29, 98, DIG.6, 100; 422/187, 193, 213; 585/323, 467, 805, 807

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
WEST, EAST

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,847,249 A [MARASCHINO] 08 December 1998, col. 6, lines 60-66; cols. 7-8.	1-5, 7-14
Y	US 5,776,320 A [MARION et al] 07 July 1998, see abstract.	1-14
Y	US 5,925,799 A [STANLEY et al] 20 July 1999, figs.5-7.	6
Y	US 5,888,355 A [MIKITENKO et al] 30 March 1999, cols. 4, 9, 10, 12, 14, 22.	1-14
A	US 5,476,978 A [SMITH, JR. et al] 19 December 1995, see entire document.	1-14
A	US 5,866,736 A [CHEN] 02 FEBRUARY 1999, see entire document.	1-14

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

24 MARCH 2001

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US00/33327

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,368,691 A [ASSELINEAU et al] 29 November 1994, see entire document.	1-14
A	US 5,969,203 A [DORBON et al] 19 October 1999, see entire document.	1-14